

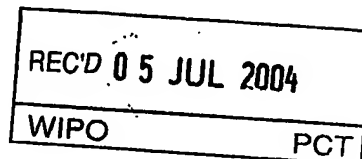
## Sertifikaat

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PATENT KANTOOR  
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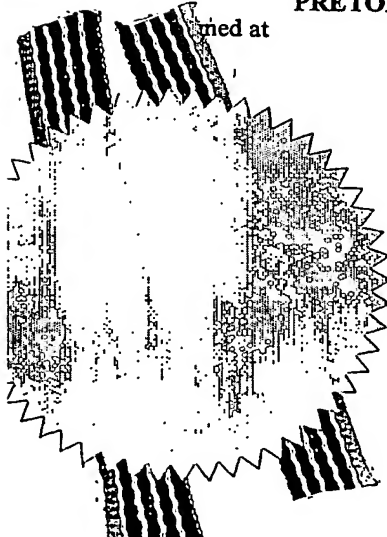
## Certificate

REPUBLIC OF SOUTH AFRICA

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This is to certify that

the documents annexed hereto are true copies of:

Application forms P.1, P2 and provisional specification of South African  
Patent Application No. 2002/10339 as originally filed in the Republic of South  
Africa on 20 December 2002 in the name of SASOL TECHNOLOGY (PTY)  
LTD for invention entitled: "TETRAMERISATION OF OLEFINS."

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Registrar of Patents

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT  
[Section 30 (1) - Regulation 22]

Revenue stamps or revenue franking machine  
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Official date stamp

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

OFFICIAL APPLICATION NO.  
21 01 **2002 / 10330**

(i) APPLICANT'S OR AGENT'S REFERENCE  
**F437**

(ii) FULL NAME(S) OF APPLICANT(S)  
71 **SASOL TECHNOLOGY (PTY) LTD**

(iii) ADDRESS(ES) OF APPLICANT(S)  
**1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA**

(iv) TITLE OF INVENTION  
54 **TETRAMERISATION OF OLEFINS**

(v) The applicant claims priority as set out on the accompanying form P2.  
The earliest priority claimed is Country: Number: Date:

(vi) This application is for a patent of addition to Patent Application No. 21 01

(vii) This application is a fresh application in terms of section 37 and is based on Patent Application No. 21 01

(viii) This application is accompanied by:

X	1.	A single copy of a provisional specification of <u>12</u> pages.
	2.	Drawings of <u>  </u> sheets
	3.	Publication particulars and abstract (form P8 in duplicate).
	4.	A copy of Figure <u>  </u> of the drawings for the abstract.
	5.	An assignment of invention.
	6.	Certified priority document(s) (state number):
	7.	Translation of the priority document(s).
	8.	An assignment of priority rights.
	9.	A copy of the form P2 and the specification of SA Patent Application No.
	10.	A declaration and power of attorney form P3.
	11.	Request for ante-dating on form P4.
	12.	Request for classification on form P9.
	13.	In terms of section 31(1) the applicant has added additional revenue stamps to this form for claiming priority after 12 months but before 15 months from the priority filing date.
X	14.	Form P2 + copy

21 01

(ix) 74 Address for service: **HAHN & HAHN INC, 222 Richard Street, HATFIELD, 0083, Pretoria**

Dated this 20 day of December 2002

*PC R L*  
Signature of applicant(s) or agent

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REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

## REGISTER OF PATENTS

OFFICIAL APPLICATION NO.		LODGING DATE: PROVISIONAL		ACCEPTANCE DATE	
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ASSIGNEE(S)				DATE REGISTERED	
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FULL NAME(S) OF INVENTOR(S)					
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PRIORITY CLAIMED		COUNTRY	NUMBER		DATE
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61					
FRESH APPLICATION BASED ON		DATE OF ANY CHANGE			

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PATENTS ACT, 1978  
**PROVISIONAL SPECIFICATION**  
[Section 30(1) - Regulation 27]

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21 01 **2002 / 10339**

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FULL NAME(S) OF APPLICANT(S)

71 **SASOL TECHNOLOGY (PTY) LTD**

FULL NAME(S) OF INVENTOR(S)

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MAHOMED, Hamdani, Ahmed; MAUMELA, Hulisani; MORGAN, David, Hedley;  
PEPLER, Lana**

TITLE OF INVENTION

54 **TETRAMERISATION OF OLEFINS**

## TETRAMERISATION OF OLEFINS

### Field of the invention:

This invention relates to an olefin tetramerisation process, a ligand for a catalyst system for tetramerisation of olefins and a catalyst system for tetramerisation of olefins.

### Background of the invention

This invention recognizes the need for a catalyst system, which facilitates the production of 1-octene in high selectivity, while avoiding the co-production of significant quantities of butenes, other octene isomers, specific higher oligomers and polyethylene. The catalyst system can also be used for the tetramerisation of other olefins, especially  $\alpha$ -olefins.

In this regard, it is known from prior art (US patent 6,184,428) that a nickel catalyst comprising a chelating ligand, preferably 2-diphenyl phosphino benzoic acid (DPPBA), a nickel precursor, preferably  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and a catalyst activator, preferably sodium tetraphenylborate, catalyse the oligomerisation of ethylene to yield a mixture of linear olefins containing considerable quantities of 1-octene. The selectivity towards linear C8  $\alpha$ -olefins is claimed to be 19%. Similarly the Shell Higher Olefins Process (SHOP process, (US patents 3,676,523 and 3,635,937) using a similar catalyst system is reported to typically yield 11 mass % 1-octene in its product mixture (Chem Systems PERP reports 90-1, 93-6 and 94/95S12).

Similarly, Ziegler-type technologies based on trialkylaluminium catalysts, independently developed by Gulf (Chevron, e.g. DE patent 1,443,927) and Ethyl Corporation (BP/Amoco, e.g. US patent 3,906,053), are also commercially used to oligomerise ethylene to mixtures of olefins that reportedly contain 13-25 mass % 1-octene (Chem Systems PERP reports 90-1, 93-6, and 94/95S12).

Moreover, chromium-based catalysts containing heteroatomic ligands with both phosphorous and nitrogen heteroatoms selectively catalyse the trimerisation of ethylene

to 1-hexene. An example of such a heteroatomic ligand for ethylene trimerisation include (o-methoxy-phenyl)<sub>2</sub>PN(Me)P(o-methoxy-phenyl)<sub>2</sub> (WO 02/04119). Since these catalyst systems are very specific for the production of 1-hexene, they only yield 1-octene as an impurity (typically less than 3 mass % of the product mixture as disclosed by WO 02/04119).

### Summary of the invention

This invention generally relates to how the need for selectively producing 1-octene from ethylene can be satisfied by using a transition metal catalyst system containing a heteroatomic ligand.

Thus, according to a first aspect of the invention there is provided a process for the tetramerisation of olefins, the process including the step of contacting the olefins with a catalyst system which includes a heteroatomic ligand and a transition metal precursor.

The term "tetramerisation" generally refers to the reaction of four monomer units to yield a linear and/or branched olefin.

By heteroatomic is meant a ligand that contains at least two heteroatoms, which can be the same or different, where the heteroatoms may be selected from phosphorus, arsenic, antimony, sulphur or nitrogen. More specifically the ligand may be described by the following general formula: (R<sup>1</sup>)(R<sup>2</sup>)A-B-C(R<sup>3</sup>)(R<sup>4</sup>), where A and C are independently phosphorus, arsenic, antimony, sulphur or nitrogen and B is a linking group between A and C. A and/ or C may be a potential donor site.

B may be any linking group, for example hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl linking groups, or inorganic linking groups, including single atom links such as -O- and -S-. B may optionally contain any additional potential donor site. Examples of B include methylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol, 1,2-dimethylhydrazine, -N(R<sup>5</sup>) where R<sup>5</sup> is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom (including silicon), a halogen, and the like. B may be -N(R<sup>5</sup>) and R<sup>5</sup> may be a hydrocarbyl or substituted hydrocarbyl.

A and C may be phosphorus.

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are each independently hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl groups. Suitable examples of  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  include, but are not limited to, methyl, ethyl, ethylenyl, propyl, butyl, cyclohexyl, benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl, dimethylhydrazyl and the like.  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may be independently aromatic or substituted aromatic groups and the substituent is not a polar group.

Any of the groups  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  may independently be linked to one or more of each other or to the linking group B to form a cyclic structure together with A and C, A and B or B and C.

The ligands can be prepared using procedures known to one skilled in the art and disclosed in published literature. Examples of ligands are:  $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(\text{phenyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(\text{benzyl})\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})_2\text{PN}(\text{cyclohexyl})\text{P}(\text{phenyl})_2$ , and  $(\text{phenyl})_2\text{PCH}_2\text{CH}_2\text{P}(\text{phenyl})_2$ ,  $(\text{phenyl})\text{SN}(\text{Me})\text{S}(\text{phenyl})$ .

The process may be a tetramerisation of  $\alpha$ -olefins.

The process may be a tetramerisation of ethylene process.

The process may include the step of combining a heteroatomic ligand with a transition metal precursor and an activator.

The transition metal may be selected from chromium, molybdenum, tungsten, titanium and nickel. Preferably, the transition metal is chromium.

The transition metal precursor which, upon mixing with the heteroatomic ligand and an activator, catalyze ethylene tetramerisation in accordance with the invention, may be simple inorganic and organic salts, for example halides, acetylacetonates, carboxylates,

oxides, nitrates, sulfates and the like, as well as co-ordination and organometallic complexes, for example, chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium hexacarbonyl, molybdenum hexacarbonyl and the like. The preferred transition metal precursor is chromium trichloride tris-tetrahydrofuran.

The process may include the step of adding a coordination complex of a heteroatomic ligand and a transition metal precursor to a reaction mixture, or the step of adding separately to the reactor, a heteroatomic ligand and a transition metal precursor such that a heteroatomic coordination complex of a transition metal is generated *in-situ*. Typically, the heteroatomic coordination complex is generated *in-situ*. The transition metal precursor, and heteroatomic ligand are combined (both *in-situ* and *ex-situ*) to typically provide metal/ligand ratios from about 0.01:100 to 10 000:1, and preferably, from about 0.1:1 to 10:1.

The heteroatomic ligand can be modified to be attached to a polymer chain (molecular wt. = 1000 or higher) so that the resulting heteroatomic coordination complex of the transition metal is soluble at elevated temperatures, but becomes insoluble at 25°C. This approach would enable the recovery of the complex from the reaction mixture for reuse and has been used for other catalyst as described by D.E. Bergbreiter *et al.*, *J. Am. Chem. Soc.*, 1987, 109, 177-179. In a similar vain these transition metal complexes can also be immobilized by binding the heteroatomic ligands to silica, silica gel, polysiloxane or alumina backbone as demonstrated by C. Yuanyin *et al.*, *Chinese J. React. Pol.*, 1992, 1(2), 152-159 for immobilizing platinum complexes.

The activator for use in the process may in principle be any compound that generates an active catalyst when combined with the heteroatomic ligand and the transition metal precursor. Mixtures of activators may also be used. Suitable compounds include organoaluminium compounds, organoboron compounds, organic salts, such as methyllithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate and the like.



Suitable organoaluminium compounds include compounds of the formula  $AlR_3$ , where each R is independently  $C_1$ - $C_{12}$  alkyl, oxygen or halide, and compounds such as  $LiAlH_4$  and the like. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), triisobutylaluminium (TIBA), tri-*n*-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes. Alumoxanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic, cages or mixtures thereof. Mixtures of different aluminoxanes may also be used in the process.

Examples of suitable organoboron compounds are boroxines,  $NaBH_4$ , triethylborane, tris(pentafluorophenyl)borane, tributyl borate and the like.

The activator may also be or contain a compound that acts as a reducing or oxidizing agent, such as sodium or zinc metal and the like, or oxygen and the like.

The activator may be selected from alkylaluminoxanes such as methylaluminoxane (MAO) and ethylaluminoxane (EAO).

The transition metal, as the precursor or a heteroatomic coordination complex, and the aluminoxane may be combined in proportions to provide Al/metal ratios from about 1:1 to 10 000:1, and preferably, from about 1:1 to 1000:1.

The process may include the step of adding to the reaction mixture a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of aluminoxane. It should however be noted that aluminoxanes generally also contain considerable quantities of the corresponding trialkylaluminium compounds used in their preparation. The presence of these trialkylaluminium compounds in aluminoxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminium compound quoted in this disclosure is additional to alkylaluminium compounds contained within the aluminoxanes.

The individual components of the catalyst system described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give an active catalyst. The mixing of the catalyst components can be conducted at any temperature between 0°C and 150°C. The presence of an olefin during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance.

The catalyst system, in accordance with the invention, or its individual components, may also be immobilized by supporting it on a support material, for example, silica, alumina, MgCl<sub>2</sub>, zirconia or mixtures thereof, or on a polymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene). The catalyst can be formed in-situ in the presence of the support material, or the support can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. In some cases, the support material can also act as or as a component of the activator. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse. The concept was successfully demonstrated with a chromium-based ethylene trimerisation catalyst by T. Monoi and Y. Sasaki, *J. Mol. Cat.A:Chem.*, 1987, **109**, 177-179. In some cases, the support can also act as a catalyst component, for example where such supports contain aluminoxane functionalities or where the support is capable of performing similar chemical functions as an aluminoxane, which is for instance the case with IOLA™ (a commercial product from Davison Catalysts).

The reaction products, or in other words olefin oligomers, as described herein, may be prepared with the disclosed catalyst system by homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated

hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, heptane, cyclohexane, 1-hexene and the like.

The process may be carried out at pressures from atmospheric to 150 barg. Ethylene pressures in the range of 10-70 bar are preferred. Particularly preferred pressures range from 30-50 barg.

The process may be carried out at temperatures from 0 °C to 250 °C. Temperatures in the range of 60-130 °C are preferred. Particularly preferred temperatures range from 80-100°C.

In a preferred embodiment of the invention, the heteroatomic coordination complex and reaction pressures is selected such that the yield of 1-octene from ethylene is greater than 25 mass %, preferably greater than 35 mass %. In this regard yield refers to grams of 1-octene formed per 100g of total reaction product formed.

Although the catalyst, its individual components, reagents, solvents and reaction products are generally employed on a once-through basis, any of these materials can, and are indeed preferred to, be recycled to some extent in order to minimize production costs.

The process may be carried out in a plant which includes any type of reactor. Examples of such reactors include, but are not limited to, batch reactors, semi-batch reactors and continuous reactors. The plant may include, in combination a) a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst system, c) effluent lines from this reactor for oligomerisation reaction products, and d) at least one separator to separate the desired oligomerisation reaction products, wherein the catalyst system may include a heteroatomic coordination complex of a transition metal salt and an activator, as described herein.

In another embodiment of the process the reactor and a separator may be combined to facilitate the simultaneous formation of reaction products and separation of these compounds from the reactor. This process principle is commonly known as reactive distillation when the reaction is a homogeneous liquid phase reaction. When the catalyst

system exhibits no solubility in the solvent or reaction products, and is fixed in the reactor so that it does not exit the reactor with the reactor product, solvent and unreacted olefin, the process principle is commonly known as catalytic distillation.

The tetramerisation process described herein may be used in a process in which tetramerisation and polymerization of ethylene occur simultaneously leading to the incorporation of the tetramerisation products into a copolymer. One example of this type of process is described in US Patent No. 5,786,431.

According to a further aspect of the invention, there is provided a catalyst system, as described above, for the tetramerisation of olefins. The catalyst system may include a heteroatomic ligand as described above and a transition metal. The catalyst system may also include an activator as described above.

According to an even further aspect of the invention, there is provided a ligand, as described above, for a catalyst system, as described above, for the tetramerisation of olefins.

## EXAMPLES OF PERFORMING THE INVENTION

The invention will now be described with reference to the following examples which are not in any way intended to limit the scope of the invention.

In the examples that follow all procedures were carried out under inert conditions, using pre-dried reagents.

### Example 1: Ethylene tetramerisation reaction using $\text{CrCl}_3(\text{tetrahydrofuran})_3$ , $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$ and MAO

A solution of 29.0 mg of  $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$  (0.073 mmol) in 5 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 80°C. The pressure reactor was

charged with ethylene after which the reactor temperature was maintained at 85°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 4.02 g of dry wax and/or polyethylene. The GC analyses indicated that the reaction mixture contained 27.84g oligomers. The product distribution of this example is summarized in Table 1.

**Example 2: Ethylene trimerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 22.4 mg of  $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$  (0.056 mmol) in 5 ml of toluene was added to a solution of 12.4 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 80°C. The procedure of Example 1 above was employed. The GC analyses indicated that the reaction mixture contained 24.31 g oligomers. The product distribution of this example is summarized in Table 1.

**Example 3: Ethylene trimerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 18.3 mg of  $(\text{phenyl})_2\text{PN}(\text{Me})\text{P}(\text{phenyl})_2$  (0.045 mmol) in 5 ml of toluene was added to a solution of 13.2 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.035 mmol) in 5 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (90ml) and MAO (methylaluminoxane, 10.6 mmol) at 80°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 85°C, while the ethylene pressure was kept at 20 barg. The procedure of Example 1 above was

employed. The GC analyses indicated that the reaction mixture contained 6.53 g oligomers. The product distribution of this example is summarized in Table 1.

**Example 4: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{benzyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 35.2 mg of  $(\text{phenyl})_2\text{PN}(\text{benzyl})\text{P}(\text{phenyl})_2$  (0.074 mmol) in 10 ml of toluene was added to a solution of 14.0 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.037 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 10.6 mmol) at 80°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 85°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 1.21 g of dry wax and/or polymer. The GC analyses indicated that the reaction mixture contained 11.78g oligomers. The product distribution of this example is summarized in Table 1.

**Example 5: Ethylene tetramerisation reaction using  $\text{CrCl}_3(\text{tetrahydrofuran})_3$ ,  $(\text{phenyl})_2\text{PN}(\text{cyclohexyl})\text{P}(\text{phenyl})_2$  and MAO**

A solution of 32.9 mg of  $(\text{phenyl})_2\text{PN}(\text{cyclohexyl})\text{P}(\text{phenyl})_2$  (0.070 mmol) in 10 ml of toluene was added to a solution of 13.54 mg  $\text{CrCl}_3(\text{tetrahydrofuran})_3$  (0.036 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (70ml) and MAO (methylaluminoxane, 10.6 mmol) at 80°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained

at 85°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax/polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 3.45 g of dry wax and/or polymer. The GC analyses indicated that the reaction mixture contained 15.72g oligomers. The product distribution of this example is summarized in Table 1.

**Table 1: Ethylene tetramerisation runs: examples 1-5**

Example	Activity	Total Product	Solids	Liquids	Liquid Product Distribution					1-Octene in C <sub>8</sub>
	g prod./g Cr	g	Wt %	Wt %	Wt %					Wt %
					C <sub>4</sub>	C <sub>6</sub>	C <sub>8</sub>	C <sub>10</sub>	C <sub>11+</sub>	
1	18570	31.9	12.6	87.4	1.8	42.3	53.6	1.1	0.2	96.0
2	16760	28.8	15.4	84.6	1.2	31.4	55.9	2.7	8.0	95.8
3	3740	6.8	4.1	95.9	1.4	26.6	42.4	2.1	24.4	95.8
4	6750	13.0	9.3	96.7	0.6	46.4	47.8	0.7	2.7	98.1
5	10240	19.2	18.0	82.0	0.4	53.4	42.9	1.0	0.8	99.0

DATED THIS 20<sup>TH</sup> DAY OF DECEMBER 2002.

  
 HAHN & HAHN INC.  
 AGENT FOR APPLICANT

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